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Proton Magnetic Relaxation of DMSO Adsorbed on NaX-Zeolite

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With 2 Figures

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Zusammenfassung

In einem Temperaturbereich zwischen 123 K und 353 K wurden die Protonen von auf NaX-Zeolith adsorbiertem Dimethylsulfoxid mit gepulster kernmagnetischer Resonanz bei 89.5 MHz untersucht. Die erhaltene magnetische T_1-Relaxationszeitkurve konnte nur mit der Annahme einer Dipol-Dipol-Wechselwirkung zwischen den Protonen der rotierenden CH_3Gruppe mit C_3-Symmetrie simuliert werden, wenn der Kernabstandsvektor eine statistische Bewegung ausführt und das Anwachsen des zweiten Moments unter 167 K mit abnehmender Temperatur in Rechnung gestellt wird. Die Kopplung mit dem Zeolithgitter verhindert, die zwei unterschiedlichen am ungestörtem DMSO-Molekül nachgewiesenen Bandlängen zwischen den C- und dem S-Atom wiederzufinden.

Introduction

The dimethylsulfoxide (DMSO) is a polar molecule with a high dielectric constant which can be used as solvent in NMR measurements when rapid proton exchange has to be suppressed. Its molecular structure is well known [1, 2]. The difference between the two S-C bond lengths were determined by pulsed NMR [3]. By means of wide band NMR [4] the calculated second moments of intramethyl, intermethyl-intramolecular and intermethyl-intermolecular interaction of protons were confirmed experimentally whith a total second moment of 25.8 G^2 at a temperature of 95 K. With increasing temperature, this second moment goes rapidly down to 8.7 G^2 at 163 K and is about 6.8 G^2 at 291.6 K (the melting point of the DMSO) indicating a free rotation of the methyl group around its C_3-symmetry axis. DMSO adsorption on solid surfaces lowers generally the number of motions and can modify the molecular structure due to the adsorbate-adsorbent interactions. The pulsed NMR technique allows mainly to gather information not only about structure changes but also about the mic-

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rodynamic behaviour of the adsorbed molecule by measuring magnetic relaxation times as a function of the sample temperature.

Experimental

A NaX-zeolite with a Si/Al ratio of 1.37 supplied by the Physics Department of the University of Leipzig was used. This zeolite as well as the employed DMSO showed no detectable EPR signal which granted a paramagnetic impurity less than 1 ppm. In order to charge the sample with dimethylsulfoxide 42 mg of degassed DMSO were adsorbed using pre-vacuum on 163 mg of pure zeolite previously dehydrated during 24 hours at 523 K. Afterwards, the sample was filtered and dried using pre-vacuum and sealed in a small glass tube.

The test equipment was a non-commercial pulse NMR spectrometer of 89.5 MHz with an electromagnet bestowed by the Volkswagenwerk Foundation. The longitudinal relaxation time T_1 was determined by two pulse sequences: $\pi - \tau - \pi/2$ and $15\pi - \tau - \pi/2$ in a temperature range between 123 K and 353 K. All experimental data for the T_1 evaluation could be well fitted by a pure exponential function.

Results

Figure 1 shows the obtained longitudinal relaxation time as a function of the sample temperature. The fitted T_1-curve has a minimum value of 147 ms at 167 K and different slopes in highest and lowest temperature regions of the measured ranges.

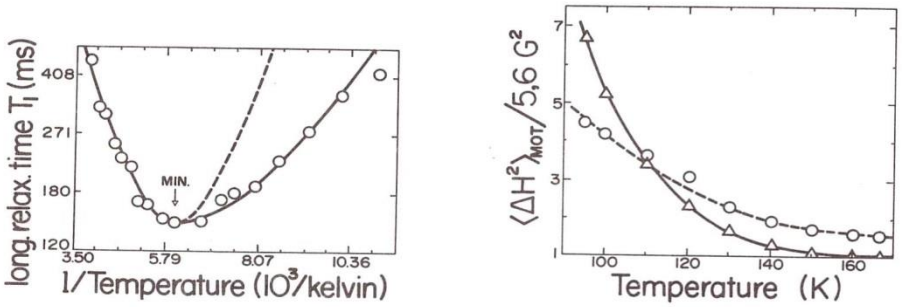

Fig. 1. Experimental T_1 data and BPP fitting (continued and dashed curves) taking into account the temperature dependence of the M_2 of the pure DMSO

Fig. 2. The comparision factor $\langle \Delta H^2 \rangle_{motion}$ / 5.6 G^2 as a function of the temperature according to DUFOURCQ (o) [4] and obtained in this work (Δ).

Theory

The microdynamic motion of an adsorbed molecule is classified between the liquid and the solid state. Starting from the fact that in solid DMSO the rotation of the methyl group is conserved up to relatively low temperatures [4] we can assume with high probability that this rotation is also mantained in the adsorption site of the dimethylsulfoxide. Then the magnetic

dipole-dipole interaction of the methyl protons of the DMSO molecule can be treated, in a first approximation, as a three spin system with equilateral geometry, with a internuclear distance of 1.78 Å and a random reorientation around the C_3-symmetry axis of the three equivalent energy positions separated by 120°. According to BPP theory [5] the rate of the longitudinal relaxation time can be expressed as:

$$\frac{1}{T_{1\,\text{intra}}} = \frac{2}{3}\gamma^2 M_2 \left[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right] \tag{1}$$

where γ is the gyromagnetic factor, ω_0 the Larmor frequency, τ_c the correlation time of the CH_3-rotation around the C_3-symmetry axis and M_2 the intramethylic second moment of DMSO. (The equation neglects tumbling [6] and tunneling effects [6, 7, 8] and intermethylic interactions [9].) Additionally, if no cross correlation effects are assumed, the intramolecular relaxation time T_1 can be depicted as follows:

$$\frac{1}{T_{1\,\text{intra}}} = \frac{1}{N}\sum_{i>j}\left[\frac{1}{T_{1\,\text{intra}}}\right]_{i,j} \tag{2}$$

where N is the proton number of the DMSO molecule and $1/T_{ij}$ the relaxation of each spin pair (i, j). Also, for a molecular rotation around a fixed axis, the second moment M_2 is [8, 9]:

$$M_2 = \langle \Delta H^2 \rangle_{\text{melting point}} = \frac{1}{4}\langle \Delta H^2 \rangle_{\text{rigid lattice}} = 179.05\, N^{-1} \sum_{i,\, j>i} \sum r_{ij}^{-6} \tag{3}$$

where r_{ij} is the distance between two protons expressed in Å. In the special case of a CH_3-rotation around its symmetry axis and a spatial random distribution of this axis:

$$\langle \Delta H^2 \rangle_{\text{r. l. intramethyl}} = \frac{9\gamma^2\hbar^2}{10r^6} = 22.6\ G^2 \tag{4}$$

and

$$\langle \Delta H^2 \rangle_{\text{melting point}} = 5.65\ G^2 \tag{5}$$

By working out of equations (3) and (4) in (1) to obtain the rate of the T_1-relaxation time, the following expression results:

$$\frac{1}{T_{1\,\text{intramethyl}}} = \frac{3\gamma^2\hbar^2}{20r^6}\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right]. \tag{6}$$

Finally, for the temperature dependence of the correlation time the Arrhenius equation was introduced.

Discussion

In Fig. 1 the best fit of the simulated relaxation time curve of the experimental data is shown using a minimization program of the standard deviation. The calculated activation energy is 7 kjoule/mol and the pre-exponential factor $\tau_0 = 2 \times 10^{-11}$ s. The experimental data agrees well with the high temperature part of the fitted T_1 curve but not with its low temperature part (dashed curve). Taking into account the temperature dependence of the second moment of the DMSO, this difference can be explained qualitatively. According to the measurements of DUFOURCQ et al. [4], the second moment varies very slowly from 8.7 G^2 to 6.8 G^2

between 167 K and 291.6 K (the melting point of DMSO). At the minimum temperature the experimentally found second moment is equal to:

$$\langle \Delta H^2 \rangle = \frac{1.05\omega_0}{\gamma^2 T_{1\,\min}} = 5.6\ G^2 . \tag{7}$$

As this value agrees well with the second moment of the intramethylic interaction in the melting point [4], we conclude that the second moment of the adsorbed DMSO has to be nearly constant in the high temperature region and corresponds to the CH_3-rotation around the C_3-axis. The slow increase of the measured total second moment by means of the wide band NMR [4] is caused by the other contributions.

In the low temperature range between 167 K and 95 K the strong elevation of the second moment generates the observed decrement of the longitudinal relaxation time. To get a better fit an exponential behaviour of the second moment of the form:

$$\langle \Delta H^2 \rangle_{\text{motion}} = 5.6\ \text{A.e}^{-\lambda T} \tag{8}$$

was used for that measured temperature range. The best result was obtained with $A = 235$ and $\lambda = 0.038$ for the interval between 95 K and 140 K, and $A = 8.96$ and $\lambda = 0.014$ for the range between 140 K and 170 K. In Fig. 1 the continued line shows the computed T_1 curve. A comparision of the temperature dependence factor:

$$F_R = \langle \Delta H^2 \rangle_{\text{motion}} / 5.6\ \text{G}^2 \tag{9}$$

between the calculated values (continued curve) and DUFOURCQ's (dashed curve) is shown in Fig. 2. This agreement becomes still better when is taken into account the increasing error of the wide band NMR data at low temperatues and the fact that the F_R factor of DUFOURCQ considers further contributions of the second moment.

Unlike the pure solid dimethylsulfoxide, the adsorbed DMSO presents only one T_1-minimum. This discrepancy may be attributed to the DMSO coupling with the zeolite lattice which disturbs the assymetric structure of the molecule, supressing the variation of the different S-C bond lengths. A continuation of this assumption can be seen by the fact that the dimethylsulfone presents no differences in these bond lengths.

Comparing again the data of the adsorbed and the unperturbed DMSO molecule it can be observed that the coupling with the zeolitic surface reduces the activation energy by half (from 14 ∓ 2 kjoule/mol to 7 kjoule/mol) and the frequency of the rotation jump by a factor of 37 (from 1.85×10^{12} Hz to 0.05×10^{12} Hz). This means that the interaction with the solid produces a hindered motion with a lowered potential barrier of rotation.

Acknowledgments

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References

[1] MARTIN, D., and H. HAUTHAL: Dimethylsulfoxide. Berlin: Akad. Verlag 1971.
[2] THOMAS, R., C. SHOEMAKER and E. KLAAS: Acta Cryst. **21** (1966) 12.
[3] PAJAK, Z., K. JURGA and S. JURGA: Acta Physica Polonica **45** (1974) 837.
[4] DUFOURCQ, J., J. CHEZEAU and B. LEMANCEAU: C.R. Academic Sc. Paris **265** (1967) 761.

[5] BLOEMBERGEN, N., E. PURCELL and R. POUND: Phys. Rev. **73** (1948) 679.
[6] STEJSKAL, E., and H. GUTOWSKY: J. Chem. Phys. **28** (1958) 388.
[7] POWLES, J., and H. GUTOWSKY: J. Chem. Phys. **23** (1955) 1692.
[8] PUNKINNEN, M.: Phys. Rev. **21** (1980) 54.
[9] WOESSNER, D.: J. Chem. Phys. **42** (1965) 1855.
[10] SMITH, G.: J. Chem. Phys. **42** (1965) 4229.
[11] POWLES, J., and H. GUTOWSKY: J. Chem. Phys. **21** (1953) 1695.